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FINE GRAINED SPUTTERING TARGETS OF COBALT AND/OR NICKEL BASE ALLOYS MADE VIA CASTING IN ISOTROPIC GRAPHITE MOLD FOLLOWED BY HOT FORGING AND ANNEALING

[0001] CROSS REFERENCE TO RELATED APPLICATIONS

[0002] This application claims priority under 35 USC 119 from U.S. Provisional Application No. 60/487,594, filed July 17, 2003, herein incorporated by reference in its entirety.

[0003] FIELD OF THE INVENTION

[0004] Sputter targets made of ferromagnetic materials are critical to thin film deposition in industries such as data storage and VLSI (very large scale integration) semiconductors. Magnetron cathode sputtering is one means of sputtering magnetic thin films.

[0005] BACKGROUND OF THE INVENTION

[0006] Typical sputtering process involves argon ion bombardment of a target as a cathode in the presence of an electric field. The dislodged atoms from the target due to ion bombardment traverse the enclosure and deposit as a thin film onto a substrate or substrates maintained at or near anode potential.

[0007] In magnetron cathode sputtering, an arched magnetic field created by magnets behind the target and formed in a closed loop over the surface of the sputter target, is superimposed on the electric field. The closed-loop leakage magnetic field traps electrons and increases the plasma density adjacent to the surface of the target, thereby significantly increasing the sputtering activity.

[0008] The use of magnetron sputtering to deposit thin films of magnetic target materials is widespread in the electronics industry, particularly in the fabrication of semiconductor and data storage devices. Due to the magnetic nature of the target materials, there is considerable shunting of the applied magnetic field in the bulk of the target. Erosion of particles from the sputter target surface generally occurs in a relatively narrow ring-shaped region corresponding to the shape of the closed-loop magnetic field.

Only the portion of the total target material in this erosion groove is consumed before the target must be replaced. The result is that typically only 18-25% of the target material is utilized. Thus, a considerable amount of material, which is generally very expensive, is either wasted or must be recycled. (In the present specification, all compositional percentages are weight percents unless otherwise indicated). Furthermore, a considerable amount of sputter deposition equipment "down-time" occurs due to frequent target replacement.

[0009] Several sputtering processes and apparatus with which the invention may be usable are disclosed in Bergmann, et al., U.S. Pat. Nos. 4,889,772 and 4,961,831; Shagun, et al., U.S. Pat. No. 4,961,832; Shimamura, et al., U.S. Pat. No. 4,963,239; Nobutani, et al., U.S. Pat. No. 4,964,962; Arita, U.S. Pat. No. 4,964,968; Kusakabe, et al., U.S. Pat. No. 4,964,969 and Hata, U.S. Pat. No. 4,971,674; and the references referred to therein; sputtering targets are discussed also in Fukaswawa, et al. U.S. Pat. Nos. 4,963,240 and 4,966,676; and Archut, et al., U.S. Pat. No. 4,966,676. These disclosures of sputtering processes and apparatus as well as sputtering targets are expressly incorporated herein by reference. Additional background on sputtering is presented by U.S. Pat. Nos. 6,402,912; 6,494,999, and 6,585,870 expressly incorporated herein by reference.

[0010] Thin films of a magnetic alloy such as Co-Ni-Pt, Co-Cr-Ni, Co-Cr-Ta, Co-Cr, Co-Ni-Cr-V, Co-Cr-Pt, or the like, formed via magnetron sputtering on a substrate are used as magnetic recording medium in magnetic disks, hard drives, magneto-optical disks. Recently, various ideas such as increasing the coercive force of the magnetic film or reducing a noise have been proposed for the magnetic recording medium to cope with high density recording.

[0011] The pass through flux (PTF) of a magnetic sputtering target is defined as the ratio of transmitted magnetic field to the applied magnetic field. A PTF value of 100% is indicative of a non-magnetic material where none of the applied field is shunted through the bulk of the target. The PTF of magnetic target materials is typically specified in the range of 0 to 100%, with the majority of commercially produced materials exhibiting values between 10 to 95%.

[0012] For magnetron sputtering, the magnetic leakage flux (MLF) or leakage magnetic field at the target surface must be high enough to start and sustain the plasma.

Under normal sputtering conditions, such as an argon pressure of 5-10 milli torr, the minimum MLF, also known as pass through flux (PTF), is approximately 150 gauss at the sputtering surface, and preferably is about 200 gauss for high speed sputtering. The magnet strength of the cathode sputtering target in part determines the MLF. The higher the magnet strength, the higher the MLF. In the case of ferromagnetic sputter targets, however, the high intrinsic magnetic permeability of the material effectively shields or shunts the magnetic field from the magnets behind the target and hence reduces the MLF on the target surface. This leads to reduced sputtering efficiency.

[0013] Because of high permeability and thus low MLF, ferromagnetic sputter targets are generally made much thinner than non-magnetic sputter targets to allow enough magnetic field to be leaked out to the sputtering surface to sustain the sputtering plasma necessary for magnetron sputtering. With some ferromagnetic materials, particularly those with higher permeability, the targets have to be machined to 0.0625 inch thick or less to achieve an MLF at the sputtering surface of 150 gauss, and some very high permeability materials are impossible to magnetron sputter because an MLF of 150 gauss simply cannot be achieved. Thus, not only can these ferromagnetic targets not simply be made thicker so as to reduce equipment down-time, they must actually be made thinner.

[0014] In general, the higher the permeability of the ferromagnetic material, the thinner the sputter target is required to be. Such a limitation on target thickness, however, leads to a shorter target life, waste of material and a need for more frequent target replacement. Furthermore, the high permeability and low MLF of a ferromagnetic target can cause problems of high impedance, low deposition rates, narrow erosion grooves, poor film uniformity and poor film performance. It is thus desirable to provide a high MLF ferromagnetic sputter target that may be made relatively thick without sacrificing film integrity.

[0015] It is well known that reducing target material permeability or increasing the target material PTF promotes less severe erosion profile, thus enhancing target material utilization during the sputtering process. This leads to a net reduction in target material cost per unit sputter fabricated product. Furthermore, the presence of severe target erosion profiles can also lead to a point source sputtering phenomena which can result in a deposited thin film that lacks thickness uniformity. Therefore, in addition to less severe

erosion profile, increasing the PTF of the target material has the added benefit of increasing the uniformity of the thickness of the deposited thin film.

[0016] Magnetic target PTF is a strong function of both target chemistry and the thermo-mechanical techniques utilized during target fabrication. For alloys that do not possess inherently high PTF as a result of their stoichiometry, i.e., PTF < 85%, it is possible to increase product PTF by various thermo-mechanical manipulations during product fabrication. For example, the typical fabrication of Ni, Co and Co-alloy targets involves casting, hot-rolling and either heat treatment or cold-rolling or a combination of heat treatment followed by cold-rolling. It is known that heat treating and cold-rolling of magnetic target materials can increase product PTF. Heat treatment of Co-Cr-Ta-(Pt) alloys below 2200° F. has been shown to increase the PTF by promoting matrix crystallographic phase transformation from face centered cubic to hexagonal closed packed as discussed in Chan et al., Magnetism and Magnetic Materials, Vol. 79, pp. 95-107 (1989).

[0017] It is suggested in Weigert et al., Mat. Sci. and Eng., A 139, p.p. 359-363 (1991), that cold-rolling of an alloy comprising 62-80 atomic % Co, 18-30 atomic % Ni, and 0-8 atomic % Cr immediately after the hot-rolling step results in an increase in product PTF. A similar result is disclosed in Uchida et al., U.S. Pat. No. 5,468,305 for an alloy containing 0.1-40 atomic % Ni, 0.1-40 atomic % Pt, 4-25 atomic % Cr and the remainder Co which is cold-rolled by not more than a 10% reduction after the hot-rolling process. Uchida et al. claim that the cold-deformation induced internal strain in the alloy reduces magnetic permeability.

[0018] High PTF in the ferromagnetic sputtering targets are generally achieved by heat treatment and/or thermal-mechanical processing treatments.

[0019] Co alloy targets strongly require the lowering in permeability. The lowering in permeability is most effective to enhance the sputtering efficiency of Co alloy targets and also greatly contributes to the reduction in cost from the viewpoint of users.

[0020] Sputtering efficiencies of targets depend on several factors such as: (a) grain size, (b) grain orientation and texture, and (c) the homogeneity of dispersion and particle size of second phase precipitates. Fine grain sizes, finely dispersed second phases in the matrix and strong texture will enhance sputtering efficiency of targets.

[0021] The effect of crystallographic orientation of a sputtering target on sputtering deposition rate and film uniformity has been described in an article by C. E. Wickersham, Jr., entitled Crystallographic Target Effects in Magnetron Sputtering in the J.Vac. Sci. Technol. A5(4), July/August 1987 publication of the American Vacuum Society.

[0022] However, there is a limit to how fine a grain size, how strong a texture, and how small a precipitate size can be achieved with conventional metal processing techniques, i.e., rolling, forging, for each metal system and alloy.

[0023] Similarly, the development of different textures and anisotropic properties by rolling is difficult. Desired plane textures and enhanced properties can be created only along the rolling direction with accompanying large reductions (see e.g., U.S. Pat. Nos. 3,954,516, 4,406,715, 4,609,408, 4,753,692 and 5,079,907 all of which are incorporated herein by reference). In addition, methods are not available which develop the required texture and anisotropy at a desired angle relative to the rolling direction at the rolling plane. Production of non-oriented textureless or isotropic products by rolling is also a difficult problem. Moreover, intensive rolling develops strongly laminated materials that often exhibit anisotropy of material properties that cannot be eliminated through existing technologies.

[0024] Grain size reduction in cobalt alloys can be achieved by thermo-mechanical processing such as hot rolling or hot forging followed by recrystallization. However, cobalt alloys containing multiple elements such as chromium, tantalum, nickel, platinum and boron are difficult to hot work by the conventional ingot metallurgy route due to segregated microstructures containing brittle second phases at the grain boundaries. Often the expensive powder metallurgy route is followed to fabricate these alloys with desirable fine and homogeneous microstructures.

[0025] To improve the performance of sputtering targets, manufacturers have used special casting techniques to reduce the resulting as-cast grain size. Also, hot or cold deformation followed by recrystallization has been used to reduce the grain size of the metal to be formed into a sputtering target.

[0026] Grain orientation control has also been suggested. A slow hot forging technique which produces a predominately <110> texture is described in U.S. Pat. No. 5,087,297 to Pouliquen incorporated herein by reference.

[0027] Conventional casting, forming, annealing, and forging techniques have produced sputtering targets with limited minimum grain sizes. Ultra-fine grains have also been achieved with a technique known as equal channel angular extrusion (ECAE), but not in production of sputtering targets. The ECAE process has been a technical curiosity but has not been used for any known commercial purpose. It is a method which uses an extrusion die containing two transversely extending channels of substantially identical cross section. It is common, but not necessary, to use channels which are perpendicular to each other, such that a cross section of the transverse channels forms an "L" shape.

[0028] Thermo-mechanical processing (i.e., various combinations of heat treatment and mechanical working) is performed on materials to refine grains and phases, change their aspect ratios, orientation and distribution, and develop substructures. Intensive plastic deformation plays an important role in thermo-mechanical materials processing. Different deformation methods are used for material processing depending upon the shape and dimensions of the billet and the initial and final properties of the material. Hot forging of metals is an advantageous method of producing sputtering materials for PVD (Plasma Vapor Deposition) targets. Hot forging also tends to produce a finer metallurgical grain size. The mechanism for this improved microstructure is dynamic recrystallization.

[0029] Dynamic recrystallization is a softening process that takes place during metal deformation at elevated temperatures. This softening is observed in a large number of metals and alloys and for numerous deformation processes. Careful analyses of the deformation behavior, including microstructural investigations, have shown that there are two broad classes of dynamic softening.

[0030] The first class is described in the literature as involving the discontinuous formation of new grains within the deformed matrix. To be more specific, grains develop during deformation by nucleation and growth, so that the average dislocation density drops, leading to significant softening. This type of dynamic recrystallization is associated with low or medium stacking fault energy metals (copper, silver, nickel, the austenite phase of conventional steels, and austenitic stainless steels).

[0031] The second class of softening process is associated with materials in which dynamic recovery is rapid enough to insure slow migration of the subgrain boundaries. Such materials undergo softening by continuous fragmentation of their substructure. This

fragmentation produces a fine grained microstructure, without involving any nucleation or growth mechanism. For these reasons, the first broad class is usually referred to as "discontinuous dynamic recrystallization," while the second is designated as "continuous dynamic recrystallization."

[0032] Traditionally, forming operations such as forging and rolling were performed on billets to develop desired physical/mechanical properties. However, in many respects, such operations are ineffective. The difficulty in achieving the high strains necessary for structure and texture formation represents the greatest limitation in these operations. In order to develop cumulative strain sufficient to provide grain refinement by recrystallization during subsequent annealing, it is necessary to apply a number of successive forging stages along the three perpendicular axes of a billet (see, e.g., U.S. Pat. Nos. 3,954,514 and 4,721,537 both of which are incorporated herein by reference). However, such a forging operation may be used only with billets having approximately equal dimensions along their three perpendicular axes. The treatment of plates by such a process results in a marked change of billet dimensions from a plate to a bar-shape (see, e.g., U.S. Pat. No. 4,511,409 incorporated herein by reference). However, conventional ingots of cobalt base alloys that are used for applications as ferromagnetic sputtering targets contain coarse, brittle intermetllic phases and hence are difficult to be deformed or strained via hot working operations.

[0033] There is a need for an improved cost effective process for making ferromagnetic sputtering targets with fine and uniform grain structure based on various cobalt based and nickel based alloys suitable for high efficiency utilization in magnetron sputtering equipment.

[0034] PREFERRED OBJECTS OF THE PRESENT INVENTION

[0035] It is a preferred object of the present invention to rapidly cast various cobalt base or nickel base alloys as plates in reusable isotropic high density graphite molds under vacuum or inert gas atmosphere.

[0036] It is another preferred object of the present invention to produce fine columnar grains parallel to the thickness of the cast plates by maintaining the thickness of the castings under 2 inch.

[0037] It is another preferred object of the invention to hot forge the cast plates containing the columnar grains along the thickness direction at in successive steps.

[0038] It is another preferred object of the invention to carry out the hot forging operations at certain combinations of temperatures and strain rates depending on the alloy composition which will cause deformation of the columnar grains followed by dynamic recrystallization into fine equiaxed grains.

[0039] SUMMARY OF THE INVENTION

[0040] The invention relates to a method of making an article of metallic alloy, comprising the steps of: melting the metallic alloy under vacuum or partial pressure of inert gas; pouring the metallic alloy into a mold with a cavity of uniform thickness, wherein the mold is machined graphite, wherein the graphite has been isostatically or vibrationally molded and has ultra fine isotropic grains having a particle size in the range of 3 to 40 microns, a density between 1.65 and 1.9 grams/cc, flexural strength between 5,500 and 20,000 psi, compressive strength between 9,000 and 35,000 psi, and porosity below 15%; solidifying the melted metallic alloy into a solid body taking the shape of the mold cavity as a plate of constant thickness; preheating the solidified plate at temperature below the melting temperature of the metallic alloy; deforming the preheated plate between two flat dies with the application of pressure along the thickness direction producing a plate with reduced but constant thickness; optionally annealing the deformed plate at temperatures below the melting temperature of the metallic alloy.

[0041] The invention typically relates to a process for making various metallic alloys based on cobalt base and/or nickel base alloys as plates with fine grain uniform microstructures that can be machined to final net shaped sizes for applications as ferromagnetic sputtering targets with high pass through flux.

[0042] This invention relates to a process for making various metallic alloys based on cobalt and nickel as plates suitable for applications as ferromagnetic sputtering targets in magnetron sputtering equipment. The invention relates to fabrication of the sputtering targets of cobalt base and/or nickel base alloys as follows:

(a) The alloys are vacuum induction melted and cast as plates with a maximum thickness of 2 inches in isotropic graphite molds under vacuum. The rectangular

plate mold geometry promotes steep thermal gradient perpendicular to the mold wall. Consequently, the directional solidification process induced by the thermal gradient leads to the formation of columnar grains with their larger axes lying parallel to the thickness of the cast plates.

(b) The cast plates are hot forged along the thickness direction under certain critical combinations of strain rate ranging between 0.1 /second to 10/second and temperature ranging between 500° F and 2200° F and total deformation ranging between 20-80 %.

(c) The forged plates are subsequently annealed within certain ranges of temperatures between 500°F to 2000°F.

[0043] Depending on the alloy compositions, the columnar grain structure of the cast plates undergoes dynamic recrystallization during the forging and/or subsequent annealing step into fine, homogeneous equiaxed grains.

[0044] More particularly, this invention relates to the use of high density ultrafine grained isotropic graphite molds, the graphite of very high purity (containing negligible trace elements) being made via the isostatic pressing route. High density (> 1.77 gm/cc), small porosity (< 13 %), high flexural strength (> 7,000 psi), high compressive strength (> 9,000 psi) and fine grains (< 10 micron) are some of the characteristics of isostatically pressed graphite that render it suitable for use as molds for casting cobalt and nickel base alloys of as much as 2 inch thickness with fine columnar grains along the thickness direction in accordance with the scope of the present invention.

[0045] The present invention has a number of preferred advantages:

(1) Casting of candidate cobalt and/or nickel base alloys in isotropic plate results into the formation of columnar grains oriented parallel to the thickness of the plates. Columnar grains have one dimension significantly larger than other dimensions. The columnar grain structure undergoes extensive deformation during high strain rate forging. The deformed grain structure concurrently recrystallizes forming new equiaxed fine grains. Equiaxed grains have approximately the same dimensions in all directions. Typically, the fine equiaxed recrystallised equiaxed grains have an average size of less than 50 microns, preferably between 10 to 30 microns.

(2) The fine grain structure of the forged and annealed plates of cobalt and nickel alloys improves properties and high efficiency performance of the sputtering targets compared to the sputtering targets of similar alloys produced by conventional processes.

(3) The high density isotropic molds can be used repeatedly many times thereby reducing significantly the cost of fabrication of the castings.

(4) The castings can be made in molds held at room or low temperatures resulting in finer grain structures and improved mechanical properties.

(5) The fine columnar grains of certain cobalt base alloys containing brittle intermetallic phases are amenable to deformation by hot forging without fracture or cracks. Large ingots produced by conventional slow cooling process contains large grains with brittle intermetallic grain boundary phases and such ingots are difficult to hot forge at high strain rate necessary to impart substantial strain energy in the alloy which triggers simultaneous grain refinement by the mechanism of dynamic recrystallization.

[0046] <u>BRIEF DESCRIPTION OF THE DRAWINGS</u>

[0047] Fig. 1 shows the microstructure of Co-16%Cr alloy cast in graphite mold and hot forged.

[0048] Figs. 2A and 2B show the uniform microstructure of the cast plate (Frig. 2A) in comparison to the segregated microstructures exhibited by a sputtering target of the same alloy made by the conventional process of ingot metallurgy followed by hot rolling (Fig. 2B).

[0049] Figs. 3A, 3B and 3C show the microstructure of the as cast plate shows fine columnar grain structure for Co-16% Cr alloy cast in graphite mold.

[0050] Fig. 4, photos (a), (b), (c) and (d) shows hot compression of the alloy of Example 6 (Example 11) at lower temperatures resulted in finer microstructures,

namelyCo-16 atomic % Cr hot compressed at (a) 2000°F, (b) 1800°F, (c) 1700°F, and (d) 1600°F.

[0051] Figs. 5A, 5B, 5C and 5D show the microstructures of the as cast nickel plate with purity of 99.95% as well as hot compressed specimens.

[0052] Fig. 6 shows the as cast dendritic microstructure of a Co-10Cr-5Ta (at. %) alloy cast in accordance with the invention in isotropic graphite mold.

[0053] Fig. 7 shows the fine grain structure of a plate of Co-10Cr-5Ta (at. %) alloy cast in isotropic graphite mold and then hot forged at 2000°F in accordance with the invention.

[0054] DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A. Graphite

[0055] Isotropic graphite is the most preferred material as the main body of the mold employed in the present invention for the following reasons:

[0056] Isotropic graphite made via isostatic pressing or vibration molding has fine isotropic grains (3 - 40 microns) whereas extruded graphite produced via extrusion from relative coarse carbon particles results in coarse anisotropic grains (400- 1200 microns).

[0057] Isotropic fine grained graphite has much higher strength, and structural integrity than other grades of graphite, such as those made by extrusion process (extruded graphite) due to the presence of extremely fine grains, higher density and lower porosity, as well as the absence of "loosely bonded" carbon particles.

[0058] Isotropic graphite produced by isostatic pressing has fine grains (3-40 microns)

[0059] Isotropic graphite has much higher strength, and structural integrity than extruded anisotropic graphite, due to absence of "loosely bonded" carbon particles, finer grains, higher density and lower porosity.

[0060] Isotropic fine grained graphite can be machined with a very smooth surface compared to extruded graphite due to its high hardness, fine grains and low porosity.

[0061] More particularly, this invention relates to the use of high density ultrafine grained isotropic graphite molds, the graphite of very high purity (containing negligible trace elements) being made via the isostatic pressing route. High density (> 1.77 gm/cc), small porosity (< 13 %), high flexural strength (> 7,000 psi), high compressive strength (> 9,000 psi) and fine grains (< 10 micron) are some of the characteristics of isostatically pressed graphite that render it suitable for use as molds. The other important properties of the graphite material are high thermal shock, wear and chemical resistance, and minimum wetting by liquid metal.

[0062] References relating to isotropic graphite include U.S. Patent Nos. 4,226,900 to Carlson, et al, 5,525,276 to Okuyama et al, and 5,705,139 to Stiller, et al., all incorporated herein by reference. See also, published U.S. patent application nos. 2004/0060685; 2004/0055725; 2004/0040690; 2004/0003913; 2003/0042001 and 2003/0029593 to Ray et al., and U.S. patent no. 6,634,413 to Ray et al, all incorporated herein by reference.

[0063] The typical physical properties of isotropic graphite made via isostatic pressing graphite are given in Table 1.

TABLE 1 –
PROPERTIES OF ISOTROPIC GRAPHITE MADE VIA ISOSTATIC PRESSING

Grade	Density (gm/cc)	Shore Hardness	Flexural Strength (psi)	Compressive Strength (psi)	Grain Size (microns)	Thermal Conductivity BTU/ft-hr-°F	Porosity (open)
R8500	1.77	65	7250	17,400	6	46	13%
R8650	1.84	75	9400	21750	5	52	12%
R8710	1.88	80	12300	34800	3	58	10%

[0064] Parameters referenced in the present specification are measured according to the following standards unless otherwise indicated.

[0065] Compressive strength is measured by ASTM C-695.

[0066] Flexural strength is measured by ASTM C 651.

[0067] Thermal conductivity is measured according to ASTM C-714.

[0068] Porosity is measured according to ASTM C-830.

[0069] Shear strength is measured according to ASTM C273, D732.

[0070] Shore hardness is measured according to ASTM D2240.

[0071] Grain size is measured according to ASTM E 112.

[0072] Coefficient of thermal expansion is measured according to E 831.

[0073] Density is measured according to ASTM C838-96.

[0074] Oxidation threshold is measured according ASTM E 1269-90.

[0075] Vickers microhardness in HV units is measured according to ASTM E 384.

[0076] B. Molding

[0077] An embodiment of the present invention is a method of making an article of metallic alloy, comprising the steps of: melting the metallic alloy under vacuum or partial pressure of inert gas; pouring the metallic alloy into a mold with a cavity of uniform thickness, wherein the mold is machined graphite, wherein the graphite has been isostatically or vibrationally molded and has ultra fine isotropic grains having a particle size in the range of 3 to 40 microns, a density between 1.65 and 1.9 grams/cc, flexural strength between 5,500 and 20,000 psi, compressive strength between 9,000 and 35,000 psi, and porosity below 15%; solidifying the melted metallic alloy into a solid body taking the shape of the mold cavity as a plate of constant thickness; preheating the solidified plate to a temperature below the melting temperature of the metallic alloy; deforming the preheated plate between two flat dies with the application of pressure along the thickness direction producing a plate with reduced but constant thickness; and annealing the deformed plate at temperatures below the melting temperature of the metallic alloy.

[0078] Typically, the melting is done by vacuum induction melting (VIM).

[0079] Preferably, the mold has a temperature in the range from 30 to 800° C when the alloy is poured into the mold. Typically, the mold has a temperature in the range from 200 to 800° C when the alloy is poured into the mold, or the mold has a temperature in the range from 100 to 500° C when the alloy is poured into the mold. Typically, the mold

cavity is round or square or rectangular with a constant thickness in the range from 0.25 to 2 inch, or from 0.5 to 2 inch, or from 0.5 to 1 inch.

[0080] C. Preheating

[0081] Typically, after molding the solidified plate is preheated before deformation at temperature in the range from 500 to 2200° F or in the range from 1000 to 2200° F, or in the range from 1000 to 2000° F or in the range from 1200 to 1800° F or in the range from 1200 to 1600° F.

[0082] D. Hot Forging

[0083] The hot forging of plates cast in graphite molds is primarily carried out in open flat dies in accordance with the present invention. The optimum forging parameters need to be determined for each alloy before the actual forging operation is carried out.

[0084] Flow stress of an alloy at a specific temperature is a fundamental characteristic of great importance. It is the stress that must be applied to make the metal deform plastically.

[0085] The control of grain size evolving during the hot forging process for cobalt and/or nickel base alloys is achieved by using a specific set of thermo-mechanical processing conditions. The starting columnar grain size produced by the casting process employed in the present invention is critical. Samples machined from each cast plate are subjected to a series of hot compression tests over a range of temperatures and strain rates. Hot compression is carried out to achieve deformation in the range, 10-80 % or 20-80% in a single step or a multiple steps at a given temperature.

[0086] Typically, the preheated plate is pressed between two flat dies at strain rate in the range from 0.1/second to 10/second, or in the range from 0.5/second to 10/second, or in the range from 1/second to 10/second, or in the range from 1/second to 5/second. Typically, the preheated plate is deformed between two flat dies undergoing 10-80 % reduction in thickness, or 20-80 % reduction in thickness, or 30-70 % reduction in thickness.

[0087] E. Annealing

[0088] Following hot compressions, the samples are annealed optionally to induce dynamic recrystallization. The microstructures including grain size and grain distribution are evaluated after hot compression and annealing treatments. Based on microstructural characteristics, the hot forging parameters are determined for each alloy.

[0089] F. Alloys

[0090] The invention is suitable for fabricating various nickel and cobalt base alloys which are suitable for applications as ferromagnetic sputtering targets in magnetron sputtering systems.

[0091] 1. Cobalt and Cobalt base alloys

[0092] The Co-base alloy used as targets for magnetron cathode sputtering contains further elements that produce intermetallic phases dispersed in the matrix. The typical chemistries of such alloys can be described by the following formula:

[0093] $Co_{1-x-y} M_x R_y$

[0094] The compositions are in atom percent, wherein M is at least one of the elements chromium, platinum, nickel, palladium or similar elements and $0<=x<=0.3$, and R is at least one of the elements tantalum, molybdenum, tungsten, boron, hafnium, niobium, vanadium or similar elements which promotes the tendency towards the formation of intermetallic phases and $0.015 <= y <= 0.20$.

[0095] Depending on the manufacturing techniques employed, the grain boundaries, twin grain boundaries or slip bands of the Co-based matrix are decorated with the elements forming the intermetallic phase.

[0096] Sputtering targets based on cobalt alloys such as Co – 30 Ni – 15 Cr (atom percent) are used for magnetic recording media production to form recording and protection films, respectively. Poor consumable volume efficiency of Co alloy targets fabricated by conventional techniques such as ingot casting and hot rolling have permeability of > 200. If the microstructure of cobalt alloys can be rendered more homogeneous and fine grained, permeability can be reduced to below 50 leading to 100 % increase in target life.

[0097] Cobalt- Iron- Boron is a family of ferromagnetic target alloys a containing various amounts of Iron (Fe) and Boron (B). Typically these amounts are approximately 10 at% Fe and 2-5 at% B.

[0098] Various other ternary and multi-component cobalt base alloy systems for sputtering target applications are listed below:

[0099] Cobalt-Iron

[00100] Cobalt-Iron-Boron

[00101] Cobalt-Iron-Chromium

[00102] Cobalt-Zirconium-Tantalum

[00103] Cobalt-Zirconium-Niobium

[00104] Cobalt-Zirconium-Rhodium

[00105] Cobalt –Platinum

[00106] Cobalt-Chromium-Platinum

[00107] Cobalt-Chromium- Platinum -Tantalum

[00108] Cobalt-Platinum-Boron

[00109] Cobalt-Chromium

[00110] Cobalt-Chromium-Nickel

[00111] Cobalt-Chromium-Tantalum

[00112] Cobalt- Niobium-Hafnium

[00113] Cobalt-Niobium-Titanium

[00114] Cobalt-Niobium-Iron

[00115] Typically the metallic alloy is a cobalt base alloy having the composition in weight percent as follows:

Cobalt	=	Balance
Chromium	=	5 to 20%
Tantalum	=	5 to15%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

[00116] Another typical metallic alloy is a cobalt base alloy having the composition in weight percent as follows:

Cobalt	=	Balance
Chromium	=	5-20%
Iron	=	0-15%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

[00117] Another typical metallic alloy is a cobalt base alloy having the composition in weight percent as follows:

Cobalt	=	Balance
Chromium	=	5-20%
Platinum	=	5-15%
Boron	=	0- 2 %

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

[00118] Another typical metallic alloy is a cobalt base alloy having the composition in weight percent as follows:

Cobalt	=	Balance
Chromium	=	0-20%
Zirconium	=	0 - 5%
Niobium	=	0 - 5%
Tantalum	=	0 -10%
Hafnium	=	0 -10%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

[00119] 2. Nickel and Nickel Alloys

[00120] Nickel and nickel alloy targets are used in magnetron sputtering process to fabricate thin films on substrates for a variety of applications such as:

[00121] Corrosion resistant film adherence to non-metals, thin film resistors, magnetic thin films, disk drives and magnetic random access memory (MRAM), contact layers and under bond metallization, ferromagnetic films and diffusion barriers.

[00122] Various ternary and multicomponent nickel base alloy systems that are currently used as sputtering targets are listed below:

High purity nickel (3N7 purity)
Nickel - Chromium.
Nickel Chromium Iron
Nickel- Iron -Rhodium
Nickel -Tungsten
Nickel- 7 weight percent Vanadium

[00123] A typical nickel base alloy has the composition in weight percent as follows:

Nickel	=	Balance
Chromium	=	0 - 20%
Iron	=	0 - 10%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

[00124] Another typical nickel base alloy has the composition in weight percent as follows:

Nickel	=	Balance
Chromium	=	0 - 20%
Rhodium	=	0 - 10%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

[00125] The nickel - tungsten alloy systems, typically consist of 10 weight percent of tungsten. The tungsten is added to make the nickel non-magnetic while retaining similar properties to pure nickel as a thin film.

[00126] A typical metallic alloy is a nickel base alloy having the composition in weight percent as follows:

Nickel	=	Balance
Chromium	=	0 - 20%
Tungsten	=	0 - 10%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

[00127] The nickel - vanadium alloy system, the desirable compositions are composed of 93 weight % nickel and 7 weight % vanadium. The vanadium is added to make the nickel non-magnetic while retaining similar properties to pure nickel as a thin film.

[00128] A typical metallic alloy is a nickel base alloy having the composition in weight percent as follows:

Nickel	=	Balance
Vanadium	=	0 - 10%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

[00129] Another suitable material is a nickel base alloy has a composition in weight percent as follows:

Nickel = 99.95 to 99.99 %.

[00130] <u>EXAMPLES</u>

[00131] <u>Example 1</u>

[00132] Table 2 lists several alloy compositions which are suitable for fabrication as sputtering targets in accordance with the scope of the present invention.

TABLE 2 (compositions are in weight %)									
Alloy No.	Ni	Co	Cr	Fe	Ta	V	Pt	B	Other
1	100								
2	80		20						
3	97					7			
4	70		20	10					
5	90								10W
6	85			10					5Rh
7	80			10					10Rh
8		90		10					
9		90		9					1 Boron
10		80	10	10					
11		83			12				5 Zr
12		90							5Nb, 5Zr
13		90	10						
14		80	10				10		
15		68	15		12		5		
16		84	16						
17	15	70	15						
18		77	10		13				

[00133] Example 2

[00134] An alloy having the composition of Co-10 atom %Cr was cast into graphite mold according to the scope of the present invention as 1 inch thick plate. Cylindrical samples (0.625 inch diameter x 1 inch long) were machined from the said cast plate. The longitudinal axis of the cylinders was parallel to the thickness direction of the plate. The cylindrical samples were hot compression tested at temperatures ranging 1600°F-2000°F to determine the optimum hot forging parameters necessary to develop fine grained microstructures.

[00135] Table 3 lists the results of hot compression tests on Co-10 atom % Cr alloy:

TABLE 3			
Test temperature (° F)	Compression ram speed	% deformation	Flow stress (ksi)
1600	3 inch / minute	31	45.29
1700	3 inch / minute	22	38.31
1800	3 inch / minute	30	39.00
1900	3 inch / minute	39	38.90
2000	3 inch / minute	38	38.34

[00136] Example 3

[00137] An alloy having the composition of Co-10Cr-5 Ta (atom %) was cast into graphite mold according to the scope of the present invention as 1 inch thick plate. Cylindrical samples (0.625 inch diameter x 1 inch long) were machined from the said cast plate. The longitudinal axis of the cylinders was parallel to the thickness direction of the plate. The cylindrical samples were hot compression tested at temperatures ranging 1900°F-2000°F to determine the optimum hot forging parameters necessary to develop fine grained microstructures.

[00138] Table 4 lists the results of hot compression tests on Co-10 Cr-5Ta alloy:

TABLE 4			
Test temperature (° F)	Compression ram speed	% deformation	Flow stress (ksi)
1900	3 inch/minute	26	78.69
1950	3 inch/minute	20	75.93
2000	3 inch/minute	29	66.46

[00139] Example 4

[00140] Pure nickel (99.95%) was cast into a graphite mold according to the scope of the present invention as 1 inch thick plate. Cylindrical samples (0.625 inch dia x 1 inch long) were machined from the cast plate. The longitudinal axis of the cylinders was parallel to the thickness direction of the plate. The cylindrical samples were hot compression tested at temperatures ranging 1200°F-2000°F to determine the optimum hot forging parameters necessary to develop fine grained microstructures.

[00141] Table 5 lists the results of hot compression tests on nickel

TABLE 5

Test temperature (° F)	Compression ram speed	% deformation	Flow stress (ksi)
1200	3 inch/minute	58	53.41
1300	3 inch/minute	43	48.43
1400	3 inch/minute	74	39.00
1700	3 inch/minute	58	35.98
1800	3 inch/minute	68	30.60
1900	3 inch/minute	55	30.26
2000	3 inch/minute	62	23.87

[00142] Example 5

[00143] An alloy having the composition of Ni-7 was cast into a graphite mold according to the scope of the present invention as 1 inch thick plate. Cylindrical samples (0.625 inch dia x 1 inch long) were machined from the said cast plate. The longitudinal axis of the cylinders was parallel to the thickness direction of the plate. The cylindrical samples were hot compression tested at temperatures ranging 1200°F-2000°F to determine the optimum hot forging parameters necessary to develop fine grained microstructures.

[00144] Table 6 lists the results of hot compression tests on Ni-7 weight % V alloy

TABLE 6			
Test temperature (° F)	Compression ram speed	% deformation	Flow stress (ksi)
1600	6 inch/minute	63	47.27
1700	6 inch/minute	57	51.25
1800	6 inch/minute	60	50.30
1900	6 inch/minute	47	29.76

[00145] <u>Example 6</u>

[00146] An alloy having the composition of Co-16 atom % Cr was cast into a graphite mold according the scope of the present invention as plates with the following dimensions: 5 x 5 x 1 inch thick plate and 4.5 x 4.5 x 1.5 inch thick plate in graphite molds.

[00147] The plates were heated to 2100°F and forged into 0.4 inch thick plates. The forged plates showed fine grained microstructures with homogeneous dispersions of fine second phase precipitates throughout the primary grains of the matrix. The forged plates were machined to final thickness of about 0.315 inch and were analyzed for the percentage PTF (pass through flux). The results are shown in Table 7 below. Also listed in the same Table 3 are the data obtained from sputtering targets having the similar compositions produced by the conventional process based on ingot melting, casting and hot rolling. The sputtering targets produced by the method disclosed in the present invention show higher PTF values compared to the similar targets produced by the conventional processes.

TABLE 7			
Composition	Produced by	Final Machined Thickness (inch)	% PTF
Co-16atom %	casting in graphite mold followed by hot forging	0.315	61
Co-16atom %	casting in graphite mold followed by hot forging	0.315	65
Co-16atom %	casting in graphite mold followed by hot forging	0.315	63
Co-16atom %	conventional ingot metallurgy and hot rolling	0.315	58
Co-16atom %	conventional ingot metallurgy and hot rolling	0.315	59

[00148] Example 7

[00149] Several cobalt base alloy compositions as listed in Table 3 below are cast into isotropic graphite molds according the scope of the present invention as plates having a thickness ranging between 1 to 2 inches.

[00150] The plates are heated between 1200° F -2150° F and forged into plates at strain rates ranging between 0.1/second to 10/second with total deformation ranging between 20 to 80 %. The forged plates show fine equiaxed grains with homogeneous dispersions of fine second phase precipitates throughout the primary grains of the matrix. The forged plates are machined to final thickness of 0.250 inch and are analyzed for the percentage PTF (pass through flux). The results are shown in Table 8 below.

TABLE 8		
Composition (atom %)	Final machined Thickness (inch)	% PTF
Co-10Cr-5 Ta	0.250	70
Co-13Cr-6Ta	0.250	68
Co-10Cr-15 Pt	0.250	70
Co-12Cr-13 Pt-10B	0.250	67
Co-10Cr-10Ni	0.250	72
Co-15Cr-15Ni	0.250	69
Co-10Cr-5 Nb	0.250	65
Co-13Cr-5 Zr	0.250	73
Co-12Cr-5Fe	0.250	70

[00151] <u>Example 8</u>

[00152] An alloy having the composition of Co-16 atom %Cr was cast into a graphite mold according the scope of the present invention as plates with the following dimensions: 5 x 5 x 1 inch.

[00153] The plates were heated to 2100°F and forged into 0.4 inch thick plates. The forged plate showed very fine grain structures as shown in Fig. 1. Fig. 1 shows the microstructure of Co-16 atomic %Cr alloy cast in graphite mold and hot forged.

[00154] <u>Example 9</u>

[00155] An alloy having the composition of Co-14Cr-4Ta (atom %Cr) was cast into a graphite mold according the scope of the present invention as plates. Figure 2 shows the uniform microstructure of the cast plate in comparison to the segregated microstructures exhibited by a sputtering target of the same alloy made by the conventional process of ingot metallurgy followed by hot rolling.

[00156] <u>Example 10</u>

[00157] An alloy having the composition of Co-16 atom %Cr was cast into a graphite mold according the scope of the present invention as plates with the following

dimensions: 5 x 5 x 1 inch. Fig. 3 illustrates the microstructure of the as cast plate shows fine columnar grain structure.

[00158] Example 11

[00159] The alloy of Example 6 cast into plates in isotropic graphite molds that were hot compressed at strain rate of 3/sec at four different temperatures, i.e., 2000°F, 1800°F, 1700°F and 1600°F. The hot compressed specimens were analyzed for microstructures. Hot compression at lower temperatures resulted into finer microstructures as revealed in Fig. 4.

[00160] Example 12

[00161] A nickel plate with purity of 99.95% was cast into a graphite mold according the scope of the present invention with the following dimensions: 5 x 5 x 1 inch. Samples sectioned from the plate were hot compressed at 3/second strain rate at various temperatures ranging from 1200°F to 1800°F.

[00162] The microstructures of the as cast plate, as well as hot compressed specimens, are illustrated in Figs. 5A, 5B, 5C and 5D. Fine grain structures resulted in samples hot compressed at lower temperatures (1200°F and 1400°F) as a result of dynamic recrystallization.

[00163] Example 13

[00164] Several nickel base alloys listed in Table 2 are cast in isotropic graphite molds into plates with thickness ranging between 0.5 to 2 inches. The plates are hot forged at strain rates between 0.1/second to 10/second at temperatures between 1200° F and 2200° F. Following forging the plates are annealed at 1200° F-2000° F for 10 minutes to 2 hours. The microstructures of the plates following forging and annealing consist of uniform fine equiaxed grains with grain size below 50 microns as a result of dynamic recrystallization.

[00165] Example 14

[00166] An alloy having the composition of Co-10Cr-5 Ta (atom %) was cast into a graphite mold according the scope of the present invention as plates with the following dimensions: 5 x 5 x 1 inch. Fig. 6 shows the as cast dendritic microstructure of the alloy.

[00167] The plate was heated to 2000°F and forged into 0.4 inch thick plates. The forged plate showed very fine grain structures as shown in Fig. 7.

[00168] It should be apparent that in addition to the above-described embodiments, other embodiments are also encompassed by the spirit and the scope of the present invention. Thus, the present invention is not limited by the above-provided description, but rather is defined by the claims appended hereto.

What is claimed is:

1. A method of making an article of metallic alloy, comprising the steps of:

melting the metallic alloy under vacuum or partial pressure of inert gas;

pouring the metallic alloy into a mold with a cavity of uniform thickness, wherein the mold is machined graphite, wherein the graphite has been isostatically or vibrationally molded and has ultra fine isotropic grains having a particle size in the range of 3 to 40 microns, a density between 1.65 and 1.9 grams/cc, flexural strength between 5,500 and 20,000 psi, compressive strength between 9,000 and 35,000 psi, and porosity below 15%;

solidifying the melted metallic alloy into a solid body taking the shape of the mold cavity as a plate of constant thickness;

preheating the solidified plate at temperature below the melting temperature of the metallic alloy;

deforming the preheated plate between two flat dies with the application of pressure along the thickness direction producing a plate with reduced but constant thickness;

optionally annealing the deformed plate at temperatures below the melting temperature of the metallic alloy.

2. The method of Claim 1, wherein the mold has a temperature in the range from 30 to 800° C when the alloy is poured into the mold.

3. The method of Claim 1, wherein the mold has a temperature in the range from 200 to 800° C when the alloy is poured into the mold.

4. The method of Claim 1, wherein the mold has a temperature in the range from 100 to 500° C when the alloy is poured into the mold.

5. The method of Claim 1, wherein the mold cavity is round or square or rectangular with a constant thickness in the range from 0.25 to 2 inch.

6. The method of Claim 1, wherein the mold cavity is round or square or rectangular with a constant thickness in the range from 0.5 to 2 inch.

7. The method of Claim 1, wherein the mold cavity is round or square or rectangular with a constant thickness in the range from 0.5 to 1 inch.

8. The method of Claim 1, wherein the solidified plate is preheated before deformation at temperature in the range from 500 to 2200° F.

9. The method of Claim 1, wherein the solidified plate is preheated before deformation at temperature in the range from 1000 to 2200° F.

10. The method of Claim 1, wherein the solidified plate is preheated before deformation at temperature in the range from 1000 to 2000° F.

11. The method of Claim 1, wherein the solidified plate is preheated before deformation at temperature in the range from 1200 to 1800° F.

12. The method of Claim 1, wherein the solidified plate is preheated before deformation at temperatures in the range from 1200 to 1600° F.

13. The method of Claim 1, wherein the preheated plate is pressed between two flat dies at strain rate in the range from 0.1/second to 10/second.

14. The method of Claim 1, wherein the preheated plate is pressed between two flat dies at strain rate in the range from 0.5/second to 10/second.

15. The method of Claim 1, wherein the preheated plate is pressed between two flat dies at strain rate in the range from 1/second to 10/second.

16. The method of Claim 1, wherein the preheated plate is pressed between two flat dies at strain rate in the range from 1/second to 5/second.

17. The method of Claim 1, wherein the preheated plate is deformed between two flat dies undergoing 10-80 % reduction in thickness.

18. The method of Claim 1, wherein the preheated plate is deformed between two flat dies to undergo 20-80 % reduction in thickness.

19. The method of Claim 1, wherein the preheated plate is deformed between two flat dies to undergo 30-70 % reduction in thickness.

20. The method of Claim 1, wherein the metallic alloy is a cobalt base alloy having the composition in weight percent as follows:

Cobalt	=	Balance
Chromium	=	5 to 20%
Tantalum	=	5 to 15%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total

21. The method of Claim 1, wherein the metallic alloy is a cobalt base alloy having the composition in weight percent as follows:

Cobalt	=	Balance
Chromium	=	5-20%
Iron	=	0-15%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

22. The method of Claim 1, wherein the metallic alloy is a cobalt base alloy having the composition in weight percent as follows:

Cobalt	=	Balance
Chromium	=	5-20%
Platinum	=	5-15%
Boron	=	0- 2 %

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

23. The method of Claim 1, wherein the metallic alloy is a cobalt base alloy having the composition in weight percent as follows:

Cobalt	=	Balance
Chromium	=	0-20%
Zirconium	=	0 - 5%
Niobium	=	0 - 5%
Tantalum	=	0 -10%
Hafnium	=	0 -10%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

24. The method of Claim 1, wherein the metallic alloy is a nickel base alloy having the composition in weight percent as follows:

Nickel	=	Balance
Chromium	=	0-20%
Iron	=	470- 10%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

25. The method of Claim 1, wherein the metallic alloy is a nickel base alloy having the composition in weight percent as follows:

Nickel	=	Balance
Chromium	=	0-20%
Rhodium	=	0-10%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

26. The method of Claim 1, wherein the metallic alloy is a nickel base alloy having the composition in weight percent as follows:

Nickel	=	Balance
Chromium	=	0- 20%
Tungsten	=	0- 10%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

27. The method of Claim 1, wherein the metallic alloy is a nickel base alloy having the composition in weight percent as follows:

Nickel	=	Balance
Vanadium	=	0-10%

and inevitable impurity elements, wherein the impurity elements are less than 0.01% each and less than 0.05% total.

28. The method of Claim 1, wherein the metallic alloy has the composition in weight percent as follows:

Nickel = 99.95 to 99.99 %.

29. A sputtering target made according to the method of Claim 1.

30. A ferromagnetic cobalt and/or nickel base alloy sputtering target having fine homogeneous equiaxed grains having a grain size less than 50 microns.

31. The target of Claim 30, further comprising homogeneous dispersions of fine second phase precipitate.

32. The target of Claim 30, having a PFT of at least 60.

33. The target of Claim 30, having a PFT of at least 65.

34. The target of Claim 30, having a PFT of about 65 to 80.

35. The target of Claim 30, having a PFT of about 65 to 75.

36. The target of Claim 30 wherein the grain size of said fine homogeneous equiaxed grains is between 10 to 30 microns.

ABSTRACT

Methods for making various nickel and cobalt base alloys into sputtering targets by melting the alloys in a vacuum or under a low partial pressure of inert gas and subsequent casting of the melt as round, square or rectangular plates in the isotropic ultra fine grained graphite molds under vacuum or under low partial pressure of inert gas are provided. The plates are subsequently preheated and deformed between two flat dies.

200 microns

Co- 16%Cr cast in graphite + hot forged

mag: 50 X

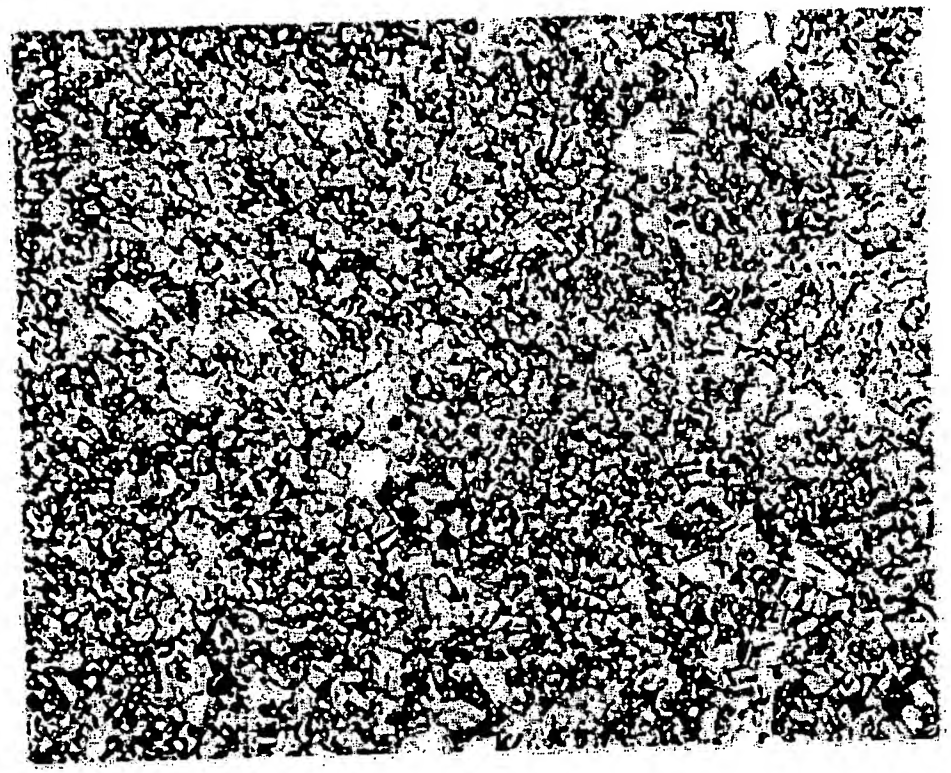
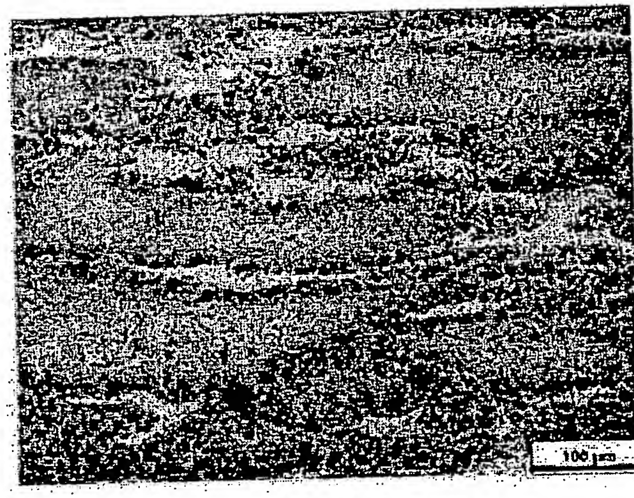


FIG. 1



Conventional process

FIG. 2B

Co-14Cr-4Ta (200 X)

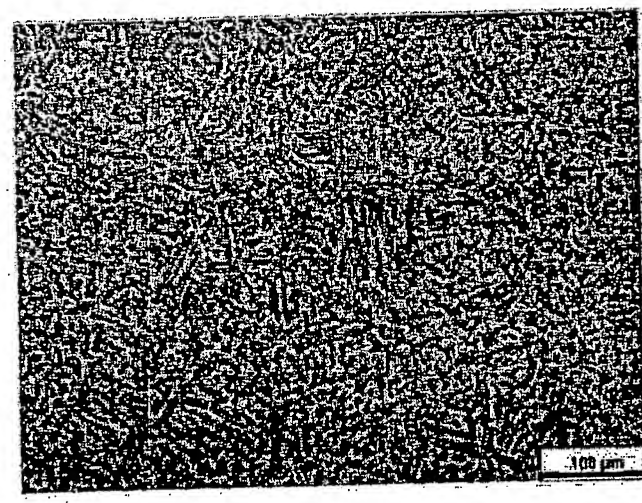


FIG. 2A

Cast in graphite mold

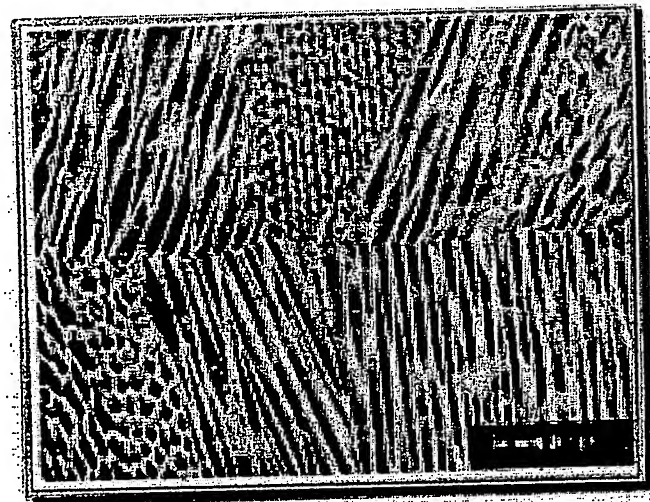


FIG. 3A

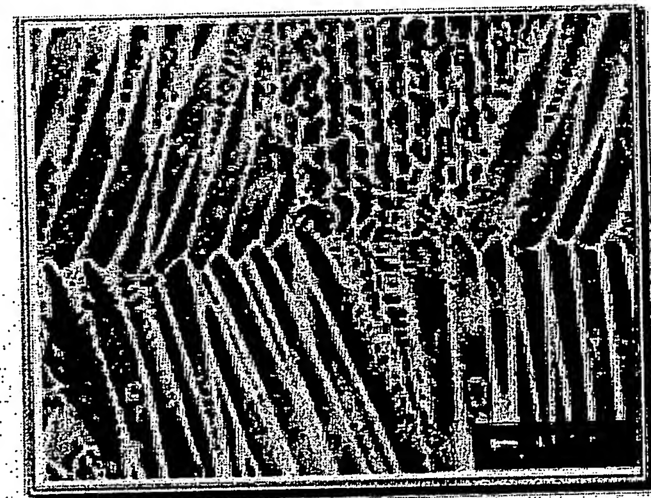


FIG. 3B

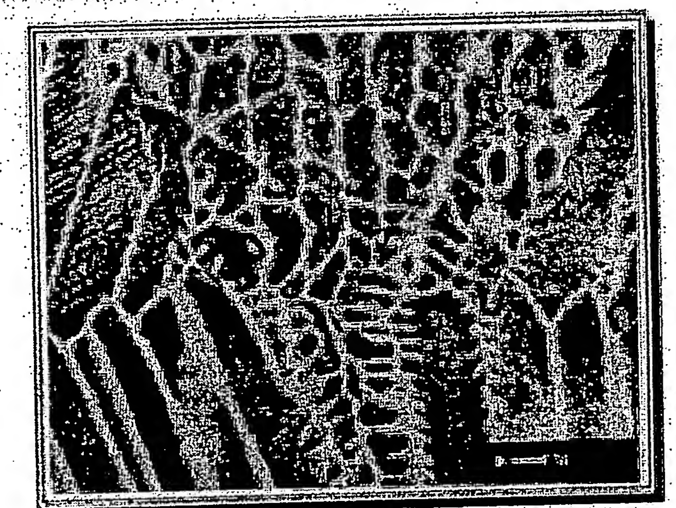


FIG. 3C

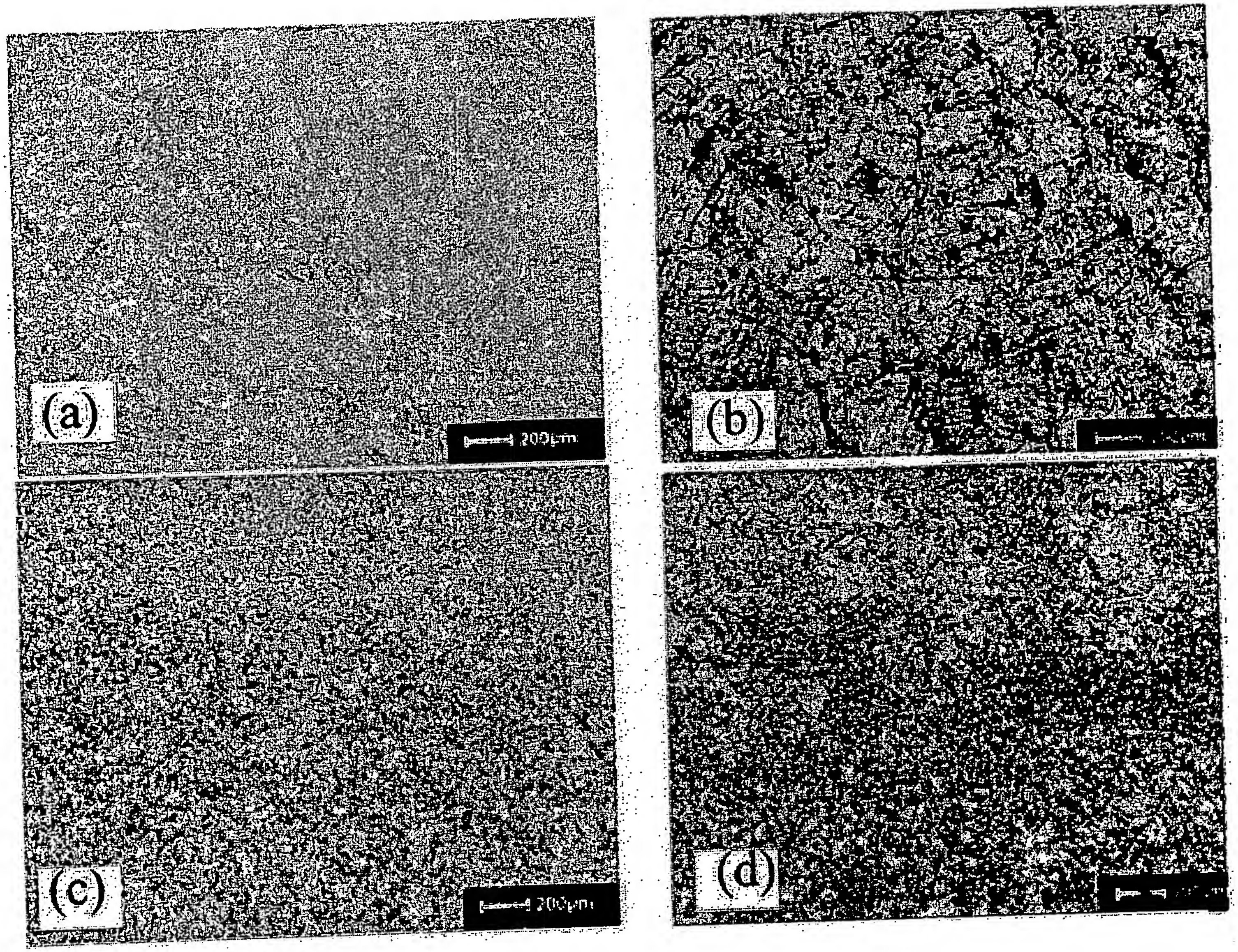


FIG. 4

FIG. 5A

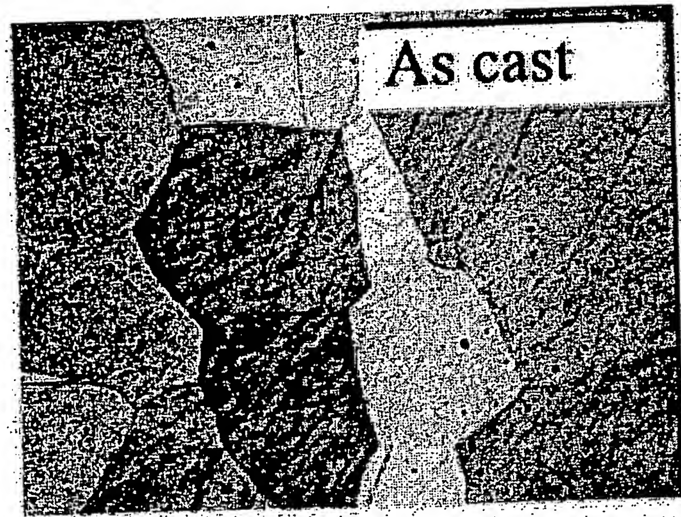


FIG. 5A

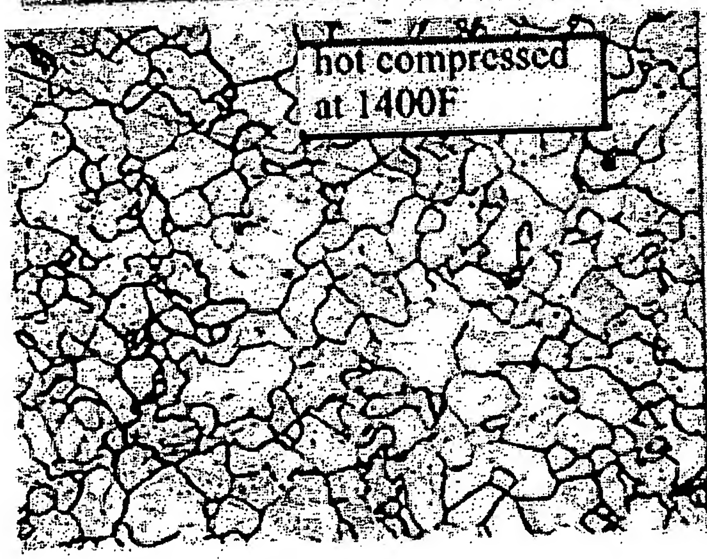


FIG. 5C

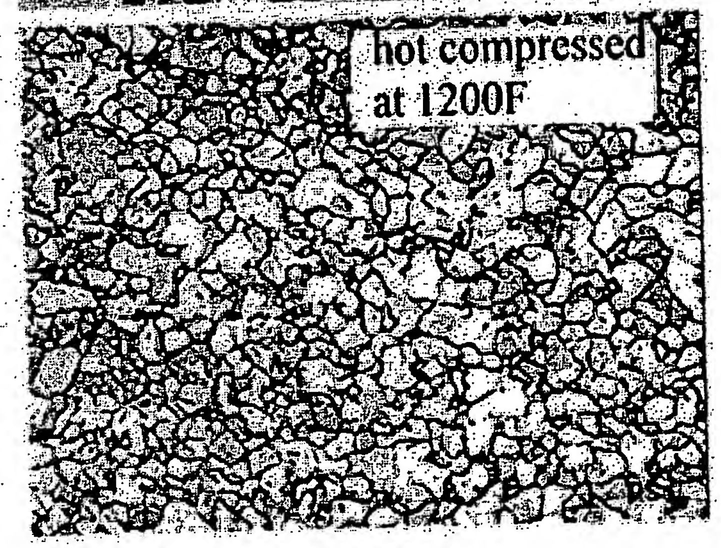


FIG. 5D

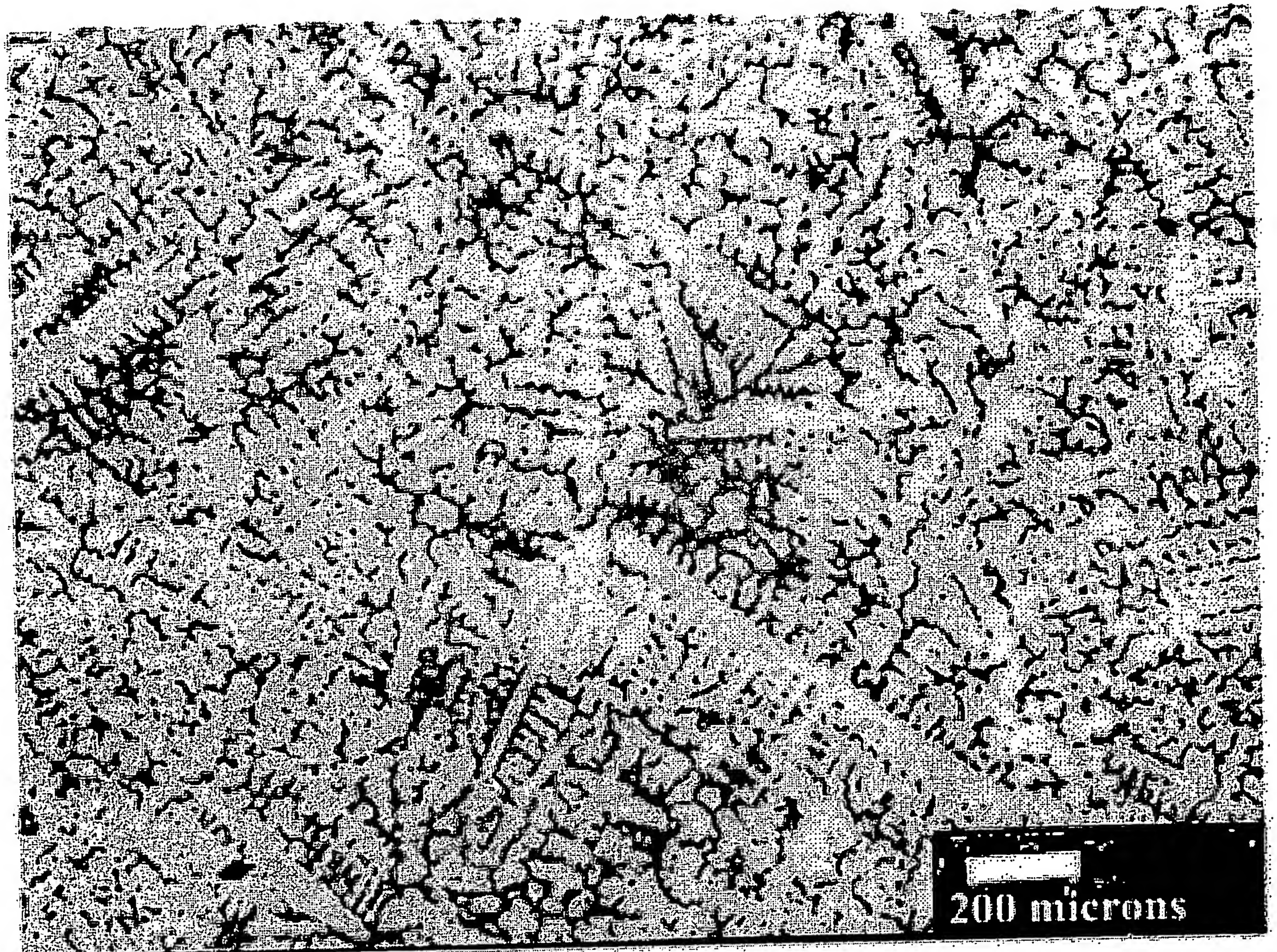


FIG. 6

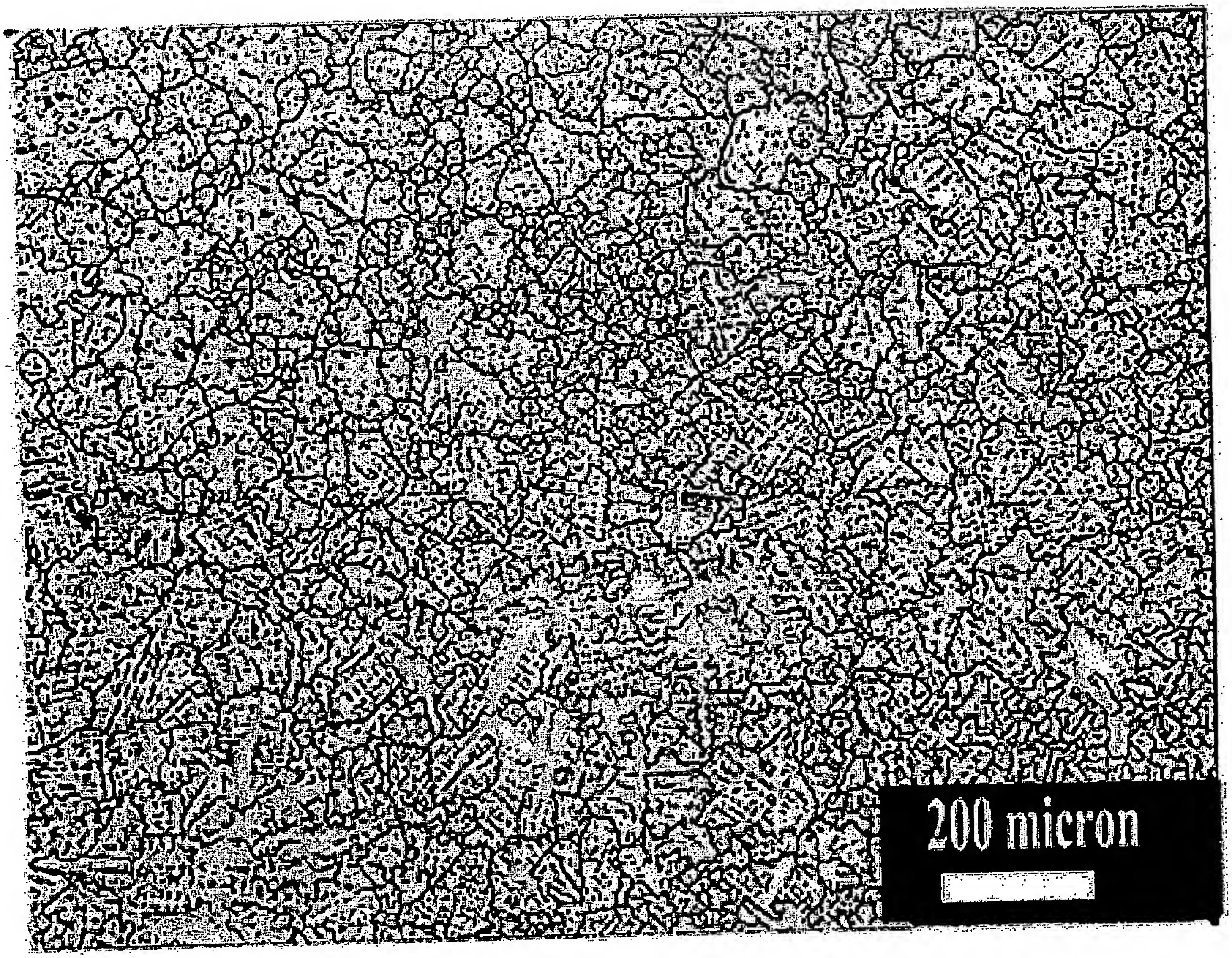


FIG. 7